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TITLE LASER DESORPTION/ABLATION STUDIES BY RESONANCE IONIZATION MASS SPECTROMETRY

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Laser Desorption/Ablation Studies by Resonance Ionization Mass Spectrometry

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ABSTRACT: Theory and results are presented for RIMS diagnostics of a variety of laser-materials interactions.

1. Introduction

Resonance ionization mass spectrometry (RIMS) is becoming an accepted tool for chemical analysis (Fassett et al 1983). The use of laser ablation or desorption coupled with RIMS detection of sputtered neutrals has a number of interesting applications and advantages: 1) the duty cycle for analytical samples is vastly improved relative to thermal evaporation (Miller et al 1982); 2) no background is introduced due to bulk heating of the sample; 3) spatial resolution is limited only by diffraction (typically ≈1 μm in diameter); 4) little sample preparation is needed; 5) sensitivity is excellent, and the detection limit frequently falls in the femtogram to attagram (absolute) or sub-ppb range; and 6) the fundamentals of laser-material interactions can be studied (Estler et al 1987).

2. Experimental

Our apparatus has been described in detail previously (Estler, et al 1987). Very briefly, desorption is initiated by pulses from a Nd^{+3}:YAG laser, operating with filled-beam optics to produce 10 nsec pulses of 1-100 mJ at 10 Hz. Ionization was affected by pulses, at variable delay, from an excimer-pumped dye laser propagating perpendicular to both the YAG laser and the flight tube of the mass spectrometer. A pair of deflection plates between the extraction [illegible] and the flight tube maximized the transmission of ions and minimized transmission variations due to velocity components perpendicular to the flight tube. Detection electronics consisted of [illegible] electron multiplier, a preamplifier, and a boxcar integrator or high-speed waveform recorder.

Results and Discussion.

A schematic of the experimental geometry is shown is Fig. 1.

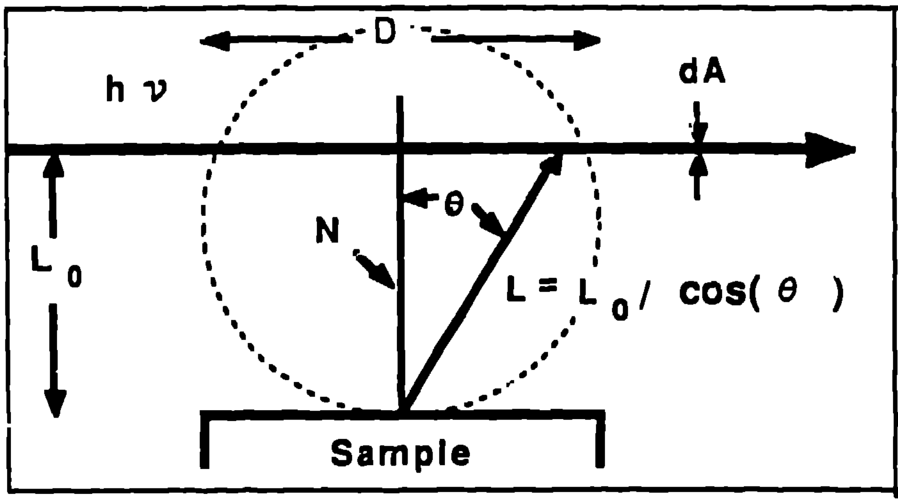

Fig. 1. Schematic of the desorption geometry L_0 is the distance from the surface to the ionization laser along the surface normal, N, and D is the distance over which constant efficiency ion collection takes place.

We have shown previously that for an isotropic [cos(Θ)], thermal distribution, the collected signal at a given linear distance (L_0) from the surface will be given by:

$$S(L_0,t) = \int S(L_0,t,\Theta)\, d\Theta \qquad [1a].$$

$$= \int C(T) \cdot (L_0^3/(\cos^2(\Theta)\, t^4)) \cdot e^{-(m(L_0/t\cos(\Theta))^2/2kT)}\, dA\,dt\,d\Theta \qquad [1b].$$

where $C(T)=\kappa C'(T)$, $C'(T)=n_0\cdot(m/2\pi kT)^{3/2}$, κ is a measure of signal collection efficiency, n_0 is the desorbed number density, the integration limits are appropriate to the apparatus, and the rest of the terms have their usual meanings. Fig. 2 shows the calculated signals for a 100 au desorbate from a 2000K surface with $L_0 = D = 1$. Note that the distributions closely simulate a single Boltzmann population, although we are integrating over a substantial angular distribution. We have used this information to quantify laser desorption measurements. In initial experiments, tantalum was desorbed from a polycrystalline Ta foil. The velocity distributions were found to be far from equilibrium ([illegible], et al 1985), with a hydrodynamic and kinetic temperature of [illegible]K, and [illegible],

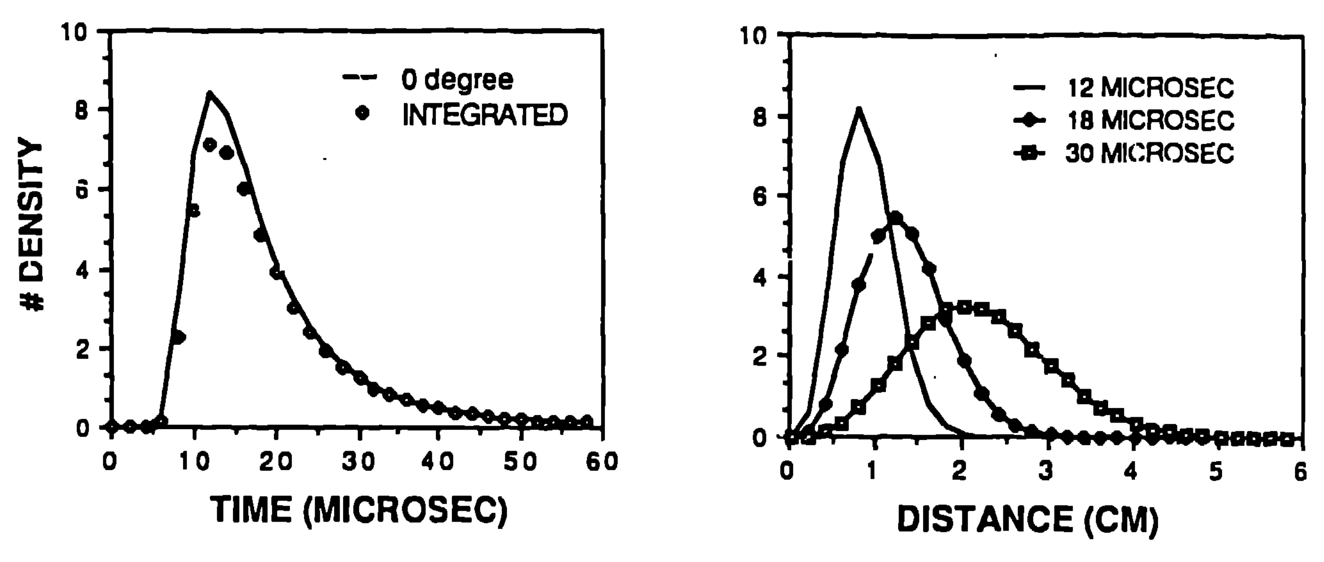

Fig. 2. Calculated temporal distributions (left) for detection at normal incidence (solid line) and integrated (diamond) over the appropriate angular distribution, and spatial distribution (right) also integrated .

respectively. The atom vapor pulse is thus temporally narrow, so that the effective duty cycle is greatly increased relative to continuous thermal desorption. The total ionization probability for the desorption/RIMS detection process is ≈2 x 10^{-4}, determined by convolving a geometric overlap of 5 x 10^{-2}, a temporal overlap of 10^{-1}, a partition function of 0.5, and an ionization/detection probability for this three-photon process of 10^{-1}.

In Al/Fe mixtures, there is a coincidence between a 1+1 ionization process for aluminum, [(4s) $^2S_{1/2} \leftarrow$ (3p) $^2P_{1/2}$ at 394.4 nm], and a variety of 2+1 ionization processes in iron, Fig. 3. This allows one to "tune" the ratio of ionization efficiencies, greatly increasing the measurement dynamic range. We were able to detect Al in iron at 1 ppt by tuning away from iron resonances, and on to the peak in the aluminum spectrum. Conversely, Fe was easily detected in Al at 10 ppm by tuning to a sharp iron feature in the aluminum spectrum tail.

We have also applied laser ablation/RIMS to the study of laser-material interactions, specifically in the optical damage process. Calcium fluoride was chosen for initial studies (Estler et al 1987). Both the velocity distributions and internal energies of the Ca and CaF ejected from the surface during breakdown (damage) were characterized. Irradiation at 1.06μ indicated thermal processes, while [illegible] nm [illegible] were highly nonthermal.

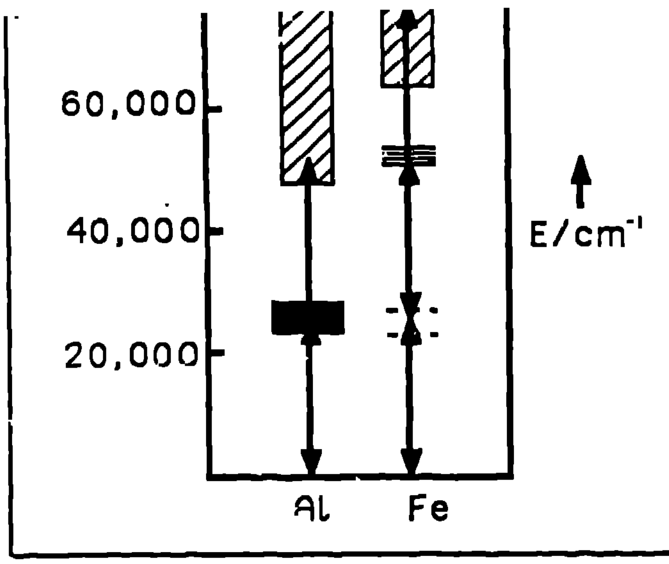

Fig. 3. Schematic energy level diagrams for Al, showing a one-photon resonance, and Fe, showing the variety of available two-photon resonances. Note that the 1+1 ionization is power broadened, while the 2+1 features in iron remain sharp

RIMS was also used in conjunction with Nomarski microscopy to characterize the initiation of optical damage in commercial optics (Estler et al 1988). The samples consisted of Sc_2O_3 /SiO_2 multilayer coatings on glass substrates. At fluences above 100 mJ/cm^2, transient iron signals were observed, with the concommitant appearance of small circular (10μ) pits in the surface. The evidence suggests that the transients were due to the presence of small, iron-containing micro-inclusions in the optical coatings. Low fluence irradiation removed near-surface contaminants with minimal damage, while higher-fluence irradiation removed more deeply imbedded, or lower susceptibility, contaminants, with simultaneous removal of surrounding coating material.

It is apparent that RIMS will play an increasingly important role in the study of the laser desorption processes, especially as surface imaging capabilities become coupled to the ionization detection.

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